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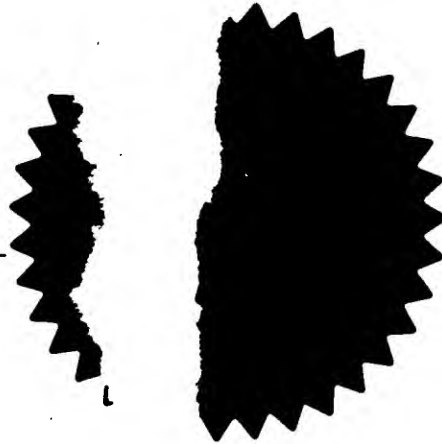
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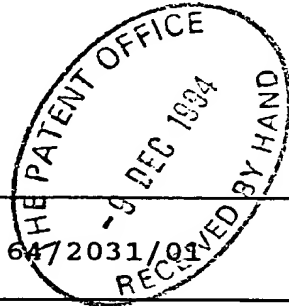
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Dated

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14DEC94 E105564-4 002890
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- 9 DEC 1994

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**The
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**Request for grant of a
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Form 1/77**

Patents Act 1977

1 Title of invention

- 1 Please give the title of the invention

Silver Plating

2 Applicant's details

- ☐ First or only applicant

- 2a If you are applying as a corporate body please give:

Corporate name Alpha Metals Limited

Country (and State Great Britain of incorporation, if appropriate)

- 2b If you are applying as an individual or one of a partnership please give in full:

Surname

Forenames

- 2c In all cases, please give the following details:

Address 1 The Broadway
Tolworth
Surrey

UK postcode (if applicable) KT6 7DQ

Country Great Britain

ADP number (if known)

6434245001

②

2d, 2e and 2f: If there are further applicants please provide details on a separate sheet of paper.

☐ **Second applicant (if any)**

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3a Have you appointed an agent to deal with your application?

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please give details below.

Agent's name

GILL JENNINGS & EVERY

Agent's address

Broadgate House
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Postcode

EC2M 7LH

Agent's ADP
number

745002

3b: If you have appointed an agent, all correspondence concerning your application will be sent to the agent's United Kingdom address.

3b If you have not appointed an agent please give a name and address in the United Kingdom to which all correspondence will be sent:

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7 The answer must be 'No' if:

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8 Please supply duplicates of claim(s), abstract, description and drawing(s).

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7 Are you (the applicant or applicants) the sole inventor or the joint inventors?

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8 Checklist

8a Please fill in the number of sheets for each of the following types of document contained in this application.

Continuation sheets for this Patents Form 1/77

0

Claim(s)

2

Description

18

Abstract

0

Drawing(s)

1

8b Which of the following documents also accompanies the application?

Priority documents (please state how many)

-

Translation(s) of Priority documents (please state how many)

-

Patents Form 7/77 - Statement of Inventorship and Right to Grant (please state how many)

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Patents Form 9/77 - Preliminary Examination/Search

-

Patents Form 10/77 - Request for Substantive Examination

-

9 Request

I/We request the grant of a patent on the basis of this application.

For the Applicant

GILL JENNINGS & EVERY

Signed

Wendy Peet.

Date 9 December 1994

(day month year)

PEET, Jillian Wendy

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SILVER PLATING

In the production of a printed circuit board (PCB), in
5 a first (multi-step) stage a "bare board" is prepared and
in a second (multi-step) stage, various components are
mounted on the board. The present invention relates to the
final steps in the manufacture of the bare board, in which
the bare board is coated with a protective layer prior to
10 passing to the second production stage.

There are currently two types of components for
attachment to the bare boards in the second stage: legged
components eg resistors, transistors etc and, more
recently, surface mount devices. Legged components are
15 attached to the board by passing each of the legs through
a hole in the board and subsequently ensuring that the hole
around the leg is filled with solder. Surface mount
devices are attached to the surface of the board by
soldering with a flat contact area or by adhesion using an
20 adhesive.

In the first stage, a board comprising an insulating
layer, a conducting circuit pattern and conductive pads
and/or through-holes is produced. The board may be a
multi-layer board having more than one conducting circuit
25 pattern positioned between insulating layers or may
comprise one insulating layer and one conducting circuit
pattern.

The through-holes may be plated through so that they
are electrically conducting and the pads which form the
30 areas to which the surface-mount components will be
attached in the subsequent component-attachment stage, are
also electrically conducting.

The conductive areas of the circuit pattern, pads and
through-holes may be formed from any conductive material or
35 mixtures of different conductive materials. They are
generally however, formed from copper. Since over time,
copper tends to oxidise to form a copper oxide layer with

poor solderability, prior to passing to the second, component-attachment stage, a protective layer is coated over the pads and/or through-hole areas where it is desired to retain solderability to prevent formation of a poorly solderable surface layer of copper oxide.

Whilst there is more than one way for preparing the bare boards, one of the most widely used processes for making the bare boards is known as the "solder mask over bare copper" (SMOBC) technique. Such a board generally comprises an epoxy-bonded fibreglass layer clad on one or both sides with conductive material. Generally, the board will be a multi-layer board having alternate conductive layers which comprise circuit pattern, and insulating layers. The conductive material is generally metal foil and most usually copper foil. In the SMOBC technique, such a board is obtained and holes are drilled into the board material using a template or automated drilling machine. The holes are then "plated through" using an electroless copper plating process which deposits a copper layer on the entirety of the board: both on the upper foil surfaces and on the through-hole surfaces.

The board material is then coated with a light sensitive film (photo-resist), exposed to light in pre-selected areas and chemically developed to remove the unexposed areas revealing the conductive areas which are the plated through-holes and pads. Generally, in the next step, the thickness of the metal foil in the exposed areas is built up by a further copper electroplating step. A protective layer of an etch resist, which is usually a tin-lead alloy electroplate composition is applied over the exposed and thickened copper areas.

The photo-resist is then removed exposing the copper for removal and the exposed copper surface is etched away using a copper etching composition to leave the copper in the circuit pattern finally required.

In the next step, the tin-lead alloy resist is stripped away.

Since components will not be attached to the copper circuit traces, it is generally only necessary to coat the solder for attaching the components over the through-hole and pad areas but not the traces. Solder mask is therefore
5 applied to the board to protect the areas where the solder coating is not required, for example using a screen printing or photo-imaging technique. The exposed copper at the holes and pads is then cleaned and prepared for solder coating and the solder-coating subsequently applied, for
10 example by immersion in a solder bath, followed by hot air levelling (HAL) to form a solder coating.

At this stage, the board comprises at least one insulating layer and at least one conductive layer. The conductive layer or layers comprise a circuit trace. The
15 board also comprises a pad or pads and/or through-hole(s) protected from tarnishing by layer of solder. A single conductive layer may comprise either a circuit trace or pad(s), or both. Any pads will be part of a conductive layer which is an outerlayer of a multi-layer board.

20 Such a board is ready to proceed to the second stage for attachment of the components. In this second stage, generally attachment of the components is achieved using solder: firstly a layer of solder paste (comprising solder and flux) is applied onto the boards, generally by printing
25 and the components are positioned on the printed boards. The board is then heated in an oven to produce fusion of the solder in the solder paste, which forms a contact between the components and the board. This process is known as reflow soldering.

30 The additional complications of attaching both legged components and the surface mount devices and the special requirements for mounting many small closely spaced components have resulted in increased demands on the surface protection coating for the conductive metal to
35 which the components will be attached, on the PCB's. It is essential that the finish applied by the bare board manufacturer does not leave a pad with an uneven surface as

this increases the risk of electrical failure. It is also essential that the protective coating does not interfere in the subsequent solder step, thereby preventing formation of a good, conducting bond between the bare board and components.

As explained above, the conductive metal surfaces are generally formed of copper and the protective surface must be applied after the first stage to prevent the formation of non-solderable copper oxide on the copper surfaces prior to the component attachment. This is particularly important because generally speaking, the first stage and the second, component-attachment stage will be carried out on completely different sites. There may therefore be a considerable time delay between formation of conducting pads and/or through holes and the component attachment stage, during which time oxidation may occur. Therefore, a protective coating is required which will retain the solderability of conducting material and enable a soldered joint to be made when the components are attached to the bare boards.

The most common protection coating presently used is tin/lead solder, generally applied using the "HAL" (Hot air levelling) process, an example of which is described in detail above.

HAL processes are limited because it is difficult to apply the solder evenly and the thickness distribution produced by the use of HAL processes makes it difficult to reliably attach the very small and closely spaced components now being used.

Several replacement treatments for the HAL coating of a solder layer are being introduced. The coatings must enable formation of a reliable electrical contact with the component. They should also be able to stand up to multiple-soldering steps. For example, as described above there are now both legged and surface mount components for attachment to the bare boards and these will generally be attached in at least two soldering operations. Therefore,

the protective coatings must also be able to withstand at least two soldering operations.

Alternatives to the tin/lead alloy solder used in the HAL process which have been proposed include organic protection, immersion tin or tin/lead plating and nickel/gold plating. In the nickel/gold process electroless plating of the copper surfaces is carried out in which a primer layer of nickel is applied onto the copper followed by a layer of gold. This process is inconvenient because there are many process steps and in addition, the use of gold results in an expensive process.

Organic protection for the copper pads during storage and assembly prior to soldering have also been effected using flux lacquer. Its use is generally confined to single-sided boards (ie. boards which have conductive pads on only one side). The coating is generally applied by dip, spray or roller coating. Unfortunately, it is difficult to provide a consistent coating to the board surfaces so limited life expectancy, due to the porosity of the coating and to its inconsistent coating thickness, results. Flux lacquers have also been found to have a relatively short shelf life. A further problem is that in the component-attachment stage, if reflow soldering is to be used to attach the components, the components are held in place on the underside of the boards with adhesive. In cases where the flux lacquer is thick, the adhesive does not bond the component directly to the printed board, but instead forms a bond between the adhesive and the lacquer coating. The strength of this bond can drop during the fluxing and soldering step causing components to be lost during contact with the solder baths.

One other alternative currently being used is passivation/protection treatment based upon the use of imidazoles or triazoles in which polymeric copper-complex compounds are formed on the copper surface. Thus, these coatings chemically bond to the surface and prevent the reaction between copper and oxygen. However this process

is disadvantageous because it tends to be inadequate for withstanding successive soldering steps so that the high temperatures reached in a first soldering step tend to destroy the layer which cannot withstand a subsequent soldering operation needed to mount further components. One example of such a process is given in EP-A-0428383, where a process is described for the surface treatment of copper or copper alloys comprising immersing the surface of copper or copper alloy in an aqueous solution containing a benzimidazole compound having an alkyl group of at least 3 carbon atoms at the 2-position, and an organic acid.

Processes are also known which provide coatings using compositions which comprise silver. For example, in GB-A-2000197 a solderable conductive layer for printed circuit boards is produced by coating a binder, containing electroconductive and soluble particles onto a substrate, leaching to form pores and subsequently immersing the coated substrate in an electroless plating bath to coat the pores with copper. In this process, the outer coating layer produced is a copper coating.

In US-A-4777078 a method is disclosed for forming copper wire patterns. The method uses an electroless copper plating bath containing silver ions which are used as a grain refiner to provide a reduction in grain size of the copper adjacent to a silver rich layer. The copper plating baths contain sodium iodide stabilising agent, silver ions, EDTA, copper sulphate and sodium hydroxide.

The three common complexing systems for electroless silver plating processes are either ammonia-based, thiosulphate-based or cyanide-based.

The ammonia systems are disadvantageous because the ammonia-containing silver solutions are unstable and explosive azides may tend to form. Thiosulphate systems are disadvantageous for use in the electronics industry because sulphur compounds in the silver coatings formed result in poor solderability so that in the subsequent

component-attachment step, a poor electrical contact may be formed between the bare board and the component.

The cyanide-based systems are disadvantageous due to the toxicity of the plating solutions.

5 In US-A-5318621 an electroless plating solution containing amino acids as rate enhancers for depositing silver or gold onto a nickel coating overlying copper on a circuit board is disclosed. It is described that neither
10 gold nor silver electroless plating baths based on thiosulphate/sulphate will plate directly onto copper because the copper rapidly dissolves without allowing a silver or gold coating to form. In the introduction of this reference, "Metal Finishing Guidebook & Directory" (1993 edition) is discussed. Silver plating solutions
15 comprising silver nitrate, ammonia and a reducing agent such as formaldehyde are mentioned.

US-A-4863766 also discloses electroless silver plating, using a cyanide-based plating solution.

20 The present invention relates to a displacement immersion silver-plating process. A displacement plating process differs from an electroless process because the silver coating forms on the surface of a metal by a simple displacement reaction due to the relative electrode potentials of the oxidisable metal of the surface to be
25 protected and of the silver ions respectively.

It is reported in for example "Modern Electroplating" by F.A. Lowenheim, published by J Wiley & Sons (1963) that silver will plate by displacement on most base metals but that immersion plated silver is poorly adherent. F.A.
30 Lowenheim suggests that when electroplating base metals with silver, it is necessary to deposit first a thin film of silver on the work-piece from a high-cyanide strike bath to ensure good adhesion of the subsequent electroplated silver layer.

35 The present invention aims to provide an alternative to the solder protection coating for the conducting surfaces of bare boards which require protection from

tarnishing between bare board manufacture and a component-attachment stage.

Surprisingly, in spite of the disclosure in "F.A. Lowenheim", the present inventors have found a method for plating by a displacement process which will provide good adhesion. The present invention overcomes the problems of the prior art silver protective coatings: ammonia, resulting in explosive solutions is not required; toxic cyanide ions can be dispensed with as no high cyanide first step is required; and a silver coating with good adhesion for PCB and solderability and providing protection against oxidation is formed.

In accordance with the present invention there is provided a process for forming a silver coating on a metal surface which is capable of being oxidised by silver ions, the process comprising in a displacement plating step, contacting the metal surface with a displacement plating composition comprising silver ions, complexing agent and having a pH of from 2 to 12.

As explained above, in the displacement process of the present invention, no additional ammonia, (which may be in the form of ammonium hydroxide), cyanide ions, formaldehyde, thiosulphate or reducing sugars are required.

The silver ions are present in the composition at a concentration of from 0.06 to 32 g/l (based on silver ions), preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.

As sources of silver ions, any water soluble silver salt may be used, for example nitrate, acetate, sulphate, lactate or formate. Preferably silver nitrate is used.

The complexing agent is preferably present in an amount of from 0.1 to 250 g/l, preferably from 2 to 200 g/l and most preferably from 10 to 100 g/l, especially around 50 g/l. The complexing agent may be any complexing agent for silver ions which does not form a water insoluble precipitate under the aqueous and pH conditions of the

composition. Mixtures of complexing agents may also be used. Examples of suitable complexing agents are amino acids preferably having at least 2 and up to 10 carbon atoms, nitrilo-triacetic acid, ethylene diamine tetracetic acid (EDTA) and N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine, citrates and/or tartrates, diethylene triamine pentaacetic acid, N-hydroxyethyl ethylene diamine triacetic acid, 1,3-diamino-2-propanol-N,N,N',N'-tetraacetic acid, N,N-di-(hydroxyethyl)glycine, bishydroxyphenylethylene diamine diacetic acid, diamino cyclohexane tetraacetic acid, ethylene glycol-bis-(8-aminoethylether)-N,N'-tetraacetic acid, gluconates, lactates, crown ethers and/or cryptands.

It may be desirable to use complexing agents which are bidentate or other multi-dentate ligands. Particularly preferred complexing agents are EDTA and N,N,N',N'-tetrakis-(2-hydroxypropyl)ethylene diamine. The complexing agent should form a soluble complex with silver ions in aqueous solution under the pH conditions of the plating solution.

The complexing agent should be either in stoichiometric equivalent amounts or in a stoichiometric excess so that all the silver ions may be complexed.

The pH of the composition may be from 3 to 10, but is preferably from 4 to 10. Thus, the composition may be acidic, up to pH 7. Alternatively, the composition may be alkaline, and have a pH of greater than 7, or even greater than 7.5.

A buffering agent may be included to ensure that the pH of the composition is within the desired range. As the buffering agent, any compatible acid or base may be included. A compatible acid or base is an acid or base which in the amounts required in the composition does not result in the precipitation out of solution of the silver ions and/or complexing agent. For example hydrogen chloride is unsuitable as it forms an insoluble silver chloride precipitate. Suitable examples include sodium or

potassium hydroxide or a carbonate salt, or where acids are required, suitable acids may include citric acid, nitric acid or acetic acid. Borates phthalates, acetates, phosphonates may be used but the buffer should not result
5 in precipitation of the metal salts and preferably does not inhibit the plating rate. An appropriate buffer will be dependent on the desired working pH.

The composition may include optional ingredients such as surfactants or wetting agents to improve the coating
10 uniformity. Where surfactants are included, preferably they are introduced into the composition in an amount such that in the plating bath, they will be present at a concentration of from 0.02 to 100 g/l. Preferably they will be incorporated at a concentration of from 0.1 to 25
15 g/l and most preferably at a concentration of from 1 to 15 g/l. Any standard surfactant or wetting agent useful in a plating bath may be used. Nonionic surfactants are preferred. Particularly preferred surfactants are alkyl phenol ethoxylates, alcohol ethoxylates and phenol
20 ethoxylates such as *Synperonic NP9 (ex ICI), *Synperonic A14 (ex ICI) and *Ethylan HB4 (ex Harcros), respectively (*denotes trade name).

A further optional ingredient which can be included in the plating baths of the present invention are grain
25 refiners. Grain refiners improve the appearance of the silver coating by causing formation of smaller crystals of silver having a more densely packed structure. Suitable examples of grain refiners include lower alcohols such as those having from 1 to 6 carbon atoms, for example
30 isopropanol and polyethylene glycols, for example PEG 1450 (Carbowax* Union Carbide). Grain refiners may be incorporated in the composition in amounts from 0.02 to 200 g/l. More preferably, if a grain refiner is included, it will be at concentrations of from 0.05 to 100 g/l and most
35 preferably from 0.1 to 10 g/l. Any non-aqueous solvent should be present in amounts below 50% by weight of the

Preferably, prior to contacting the metal surface with the displacement coating composition in the plating step, the metal surface is cleaned in the conventional way. Generally cleaning will be using an acidic cleaning composition, such as any cleaning composition well known in the art. Examples are copper conditioner PC 1144 supplied by Alpha Metals Limited.

Where there is a cleaning step using an acidic cleaning solution, generally there will be a rinsing step prior to contacting the metal surface with the plating solution.

Optionally, there may also be a micro-etching step either combined with or after the cleaning step in which the metal surface is contacted with, for example sodium persulphate solution to remove any surface copper oxide. Where such a micro-etching step is carried out, preferably there will be a subsequent acid rinse, using sulphuric acid to remove traces of cleaning and/or microetching composition.

Contact of the metal surface with the plating solution will generally be at temperatures of from 10 to 60°C. For example, the temperature of contact with the plating solution will be from 15 to 50°C, most usually from 20 to 40°C.

Contact can be by any method, usually dip, spray or horizontal immersion coating. Spray coating is preferred. Such contact may be part of a substantially continuous coating process.

The contact time of the plating solution with the metal surface is sufficient to form a silver surface over the metal. Generally the contact time will be from 10 seconds to 10 minutes. A contact time of less than 10 seconds has generally been found to give insufficient coverage with silver coating and although the contact time may be longer than 10 minutes, no additional benefit has been found from a contact time of longer than 10 minutes.

composition, preferably below 30% by weight or even below 10% or 5% by weight of the plating composition.

A further optional ingredient which may be included in the plating composition of the present invention are
5 tarnish inhibitors. Inhibitors may be incorporated in amounts of from 0.001 to 50 g/l, preferably from 0.01 to 25 g/l and most preferably from 0.05 to 10 g/l. Suitable inhibitors are described in more detail in our co-pending application filed today under our reference number
10 64/2045/01.

Other non-active, non-interfering components may be included such as defoamers especially for spray applications (eg, A100 supplied by Dow), dyes etc.

The balance in the composition is water. Deionised
15 water or other purified water which has had interfering ions removed, is used in the plating composition used in the process of the invention.

In order to form the plating composition for use in the process of the present invention, preferably a solution
20 is firstly prepared comprising deionised water, complexing agent as defined above, and any buffering agent, optionally with the other optional ingredients, and silver is added as an aqueous solution to the other components which have been formed into a pre-mix. It has been found that this is the
25 most advantageous way to prepare the solution because adding the silver in the form of a salt and trying to dissolve that directly into the plating composition is relatively time consuming and tends to be more vulnerable to photo-reaction which results in precipitation of silver
30 ions out of solution, as a dark precipitate.

Preferably the pH of the composition to which the silver salt is added will be from pH 3 to 10, most preferably from 4 to 8.

The components are mixed until they have substantially
35 dissolved. The use of heat is disadvantageous because again, it may tend to cause the formation of a dark silver precipitate.

The displacement plating process is an immersion displacement process and not a true electroless plating process. The plating compositions of the present invention are more stable than plating compositions for use in electroless systems which include for example formaldehyde. In the plating solutions of the present invention, metal atoms on the surface of the metal are oxidised by the silver ions in the solution, so that a layer of silver metal deposits on the surface of the metal surface. The process is self-limiting because when silver metal covers all of the surface sites of metal oxidisable by silver, no further reaction and therefore no further silver deposition occurs.

The present inventors have found that the rate of the displacement process may be important when a strongly adherent layer of silver is required. The presence of the complexing agent is essential to ensure that the rate of the displacement reaction is not too rapid. When the rate of the displacement reaction proceeds too quickly, the silver layer formed on the metal surface may tend to be porous, uneven and/or exhibit poor adhesion. In accordance with the present invention, the complexing agent in the plating solution ensures that the reaction proceeds at a rate sufficient to form an adherent coating, and in addition one which has good adhesion and where the silver layer forms a protective layer, gives good protection over the metal surface to prevent the formation of oxides or other tarnish. The coating thickness of the silver coating formed according to the present invention will generally be no greater than $2\mu\text{m}$.

The invention has been found to be particularly advantageous for forming a protective silver layer on PCBs, as a replacement for the HAL process described above. In addition to the good adhesion which is required in this application, the invention is particularly advantageous as it enables good solderability of the pads and/or through holes of the PCB to be retained. Therefore, in a preferred

aspect of the invention, the metal surface comprises pads and/or through holes of a PCB. The conductive metal pads and/or through-holes which are contacted with the plating composition in the process of the present invention may
5 have been formed by any process for forming pads and/or through-holes. A particularly preferred metal surface for the process of this invention is a metal surface comprising copper.

After contact of the bare board with the displacement
10 plating composition, the board is dried. Preferably, there will be a post-rinse step between contact of the board with the immersion composition and drying.

Drying may be by any means, but is generally using warm air, for example treated metal may be passed through
15 a drying oven.

The coating obtained using the method of the present invention produces a surface which is considerably more uniform and even than that obtained in the conventional HAL processes and, compared with organic protection, the
20 coating is more resistant to soldering operations. Furthermore, the process of this invention is less expensive and simpler than use of the nickel/gold process.

In the subsequent component-attachment stage, the components are soldered onto the bareboard and the metal of
25 the pad(s) and/or through-holes (generally copper) and silver may tend to intermix, but the bond formed with the components has good electrical conductivity and good bond strength.

After component attachment, finished boards having
30 components attached over the plated layer of the present invention, do not suffer joint reliability problems as do those boards formed using a nickel/gold step.

In a particularly preferred embodiment of the invention, an oxidation inhibitor is contacted with the
35 pads and/or through-holes either by incorporating a tarnish inhibitor in the plating solution or, by contact with a solution comprising tarnish inhibitor as a post-rinse step,

after the plating step, prior to attachment of the components. Where contact with the oxidation inhibitor is in a subsequent post-rinse step by contact with a solution comprising tarnish inhibitor, there may be intermediate
5 rinse and/or drying steps as described above. The use of such an tarnish inhibitor is advantageous as it inhibits tarnish formation on the protective plating.

Example 1

A composition was prepared in which 50g EDTA and 20.4g
10 of solid sodium hydroxide were mixed with sufficient water to dissolve them. A solution comprising 1g silver nitrate in deionised water was subsequently added to the premixture comprising EDTA and sodium hydroxide solution and deionised water was added to 1 litre. Copper double sided circuit
15 boards, having a variety of surface mount feature and plated through holes of various diameter were coated with the silver solution using the following procedure.

Boards were degreased with IPA, then microetched in an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_8$ (5% w/w), H_2SO_4 5% w/w for 1
20 minute. A tap water rinse for 1 minute was then employed followed by an acid rinse in H_3PO_4 5% w/w, Synperonic NP9 0.1% for 1 minute. Boards were given a further water rinse then immersed while still wet into the silver plating composition for 3 minutes at room temperature (20°C). Upon
25 removal from the silver bath, boards were rinsed for 1 minute with water and warm air dried. The copper areas were coated with a thin even silver deposit.

Coated boards were subjected to three passes through a typical IR solder paste reflow profile - see figure 1
30 (which illustrates a suitable example of temperature against time for a reflow pass), then wave soldered using NR300, an Alpha Metals VOC free, no clean flux. 100% filling of the plated-through holes with solder was achieved.

35 Further boards were stored in a humidity cabinet at 40°C/93% RH for 24 hours before being passed through 3 IR reflow profiles. These boards showed a slight degree of

tarnishing on the silver coating. However 100% hole filling was still achieved during subsequent wave soldering with NR 300 flux.

Example 2

5 A plating bath was prepared by dissolving 40g of N,N,N',N' - tetrakis-(2-hydroxypropyl)ethylene diamine and 10g of citric acid in 800cm³ of deionised water. To this solution was added a solution of 1g silver nitrate in 100cm³ of deionised water. The pH of this solution was
10 adjusted to pH 8 by addition of NaOH, then made up to 1 litre with deionised water.

Copper coupons (5cm x 5cm x 0.1cm) were silver plated in the above bath composition using the procedure as described in example 1. An adherent, thin silver coating
15 was produced.

Example 3

A bath was prepared by dissolving 50g of citric acid in 800cm³ of deionised water. To this solution was added a solution of 1g silver nitrate in 100cm³ deionised water.
20 The pH was adjusted to 4.0 with sodium hydroxide, and the bath made up to 1 litre with deionised water.

Copper coupons were silver plated using the procedure described in example 1. A thin, adherent silver coating was produced.

25 Example 4

A silver plating bath was prepared by dissolving 60g of tartaric acid in 800cm³ of deionised water. To this solution was added a solution of 1g silver nitrate in 100 cm³ of deionised water. The pH of the solution was
30 adjusted to pH 4 by addition of sodium hydroxide and the volume made up to one litre with deionised water. Copper coupons were silver plated using the procedure described in example 1. A thin, adherent silver coating was produced.

Example 5

35 A silver plating solution was prepared by forming a solution comprising 50g EDTA, 20.4g NaOH, 10g Synperonic NP9 (ICI), 3g Crodamet 02 (Croda Chemicals) in 800mls

deionised water. To this solution was added a solution of 1g AgNO₃ in 100 mls deionised water. The pH was adjusted to 7 by addition of dilute NaOH/HNO₃, then made up to 1 litre with deionised water.

5 Double sided bare copper boards were coated with the above solution using the procedure as described in example 1. 100% filling of plated through holes with solder was achieved during wave soldering with NR300 flux after passage through 3 IR reflow profiles.

10 Boards stored at 40°C/93%RH for 24 hours prior to passage through 3 IR reflow profiles showed no evidence of tarnishing and soldered well during wave soldering trials, giving 100% hole filling.

Example 6

15 Double sided bare copper boards were coated using the bath composition and procedure as described in example 1. Following removal of the boards from the silver plating solution and rinsing, the boards were immersed in a solution of 4g Reomet 42 (Ciba-Geigy) in 1 litre deionised water (pH 7) for 1 minute at room temperature. The boards were then rinsed in tap water and warm air dried. A bright even silver coating was produced.

The coated boards were stored at 40°C/93% RH for 24 hours then passed through 3 IR paste reflow profiles. The boards showed no evidence of tarnishing, and soldered well when wave soldered using NR 300 flux.

Example 7

Coupons of copper strip (5cm x 1cm) were coated with the various silver coatings as described in examples 1, 5 and 6. In addition, further samples were coated with a commercially available immersion Sn coating and two competitors solderability preservative coatings based on substituted benzimidazole chemistry. The coupons were subjected to a variety of pre-treatments - reflow passes and storage at 40°C/93% RH - then soldered using a meniscograph with NR 300 flux.

The meniscograph test method monitors the solderability by measuring the net force acting between specimen and solder. The coatings are assessed by the length of time to reach equilibrium wetting force, and the size of the equilibrium wetting force. To achieve good results in wave soldering a short wetting and high equilibrium wetting force are preferred.

The table below shows the wetting times in seconds and wetting forces after 2 seconds immersion in arbitrary units for various copper coated samples.

TABLE 1

Coating	Treatment	Wet time/sec	Wet force/ Arb.Unit
Example 1	as prepared	0.6	0.32
Example 1	3 reflow passes	0.7	0.26
Example 1	18hrs 40°C/93% RH 0 reflows	0.65	0.30
Example 1	18hrs 40°C/93 3 reflows	0.95	0.17
Example 5	as prepared	0.6	0.31
Example 5	3 reflows	0.7	0.31
Example 5	16hrs 40/93 3 reflows	0.7	0.28
Example 5	17 days 40°C/93% RH	1.7	0.12
Example 5	17 days 40/93 3 reflows	1.9	0.04
Example 6	as prepared	0.7	0.29
Example 6	3 reflows	0.7	0.25
Example 6	10 days 40/93 3 reflows	0.9	0.28
Sn	as prepared	0.95	0.34
Sn	3 reflows	> 5s	- 0.24
Sn	18 hrs 40/93 0 reflows	> 5	- 0.2
Sn	18 hrs 40/93 3 reflows	> 5	- 0.42
Benzimid A	3 reflows	0.9	0.19
Benzimid B	as prepared	0.8	0.28
Benzimid B	1 reflow	0.95	0.26

As can be seen from above, the silver coatings have shorter wetting times and higher wetting forces than the Sn and benzimidazole alternative and retain these properties more readily after humidity and heat treatment.

CLAIMS

1. A process for forming a silver coating on a metal surface comprising a metal which is oxidisable by silver ions, the process comprising contacting the metal surface with a displacement coating composition comprising silver ions, complexing agent and having a pH of from 3 to 10, in a displacement plating step.
2. A process according to claim 1 in which the process is for forming a protective coating on a metal surface comprising conductive metal pads and/or through-holes of a bare board.
3. A process according to claim 1 or claim 2 in which the metal surface comprises copper.
4. A process according to claim 1 in which the silver ions are present in the displacement coating composition at a concentration of from 0.06 to 32 g/l, preferably from 0.1 to 25 g/l, most preferably from 0.5 to 15 g/l.
5. A process according to any preceding claim in which the complexing agent is present in an amount of from 0.1 to 250 g/l, preferably from 10 to 100 g/l.
6. A process according to any preceding claim in which the displacement plating composition additionally comprises a buffering agent.
7. A process according to any preceding claim in which the displacement plating composition comprises surfactant, wetting agent, stabiliser, grain refiner and/or tarnish inhibitor.
8. A process according to claim 7 in which surfactant is incorporated in the displacement plating composition at a concentration of from 1 to 15 g/l.
9. A process according to claim 7 or claim 8 in which a grain refiner is present in the composition in an amount of from 0.05 to 100 g/l.
10. A process according to any of claims 7 to 9 in which an inhibitor is incorporated in the composition in an amount of from 0.01 to 25 g/l.

11. A process according to any preceding claim in which contacting the metal surface with the displacement coating composition is by spraying, or dip-coating in an immersion bath.
- 5 12. A process according to any preceding claim in which the metal surface is contacted with the immersion coating composition for from 10 seconds to 10 minutes, preferably at a temperature of from 10 to 60°C, most preferably at a temperature of from 15 to 50°C.
- 10 13. A process according to any preceding claim in which prior to the immersion plating step, the metal surface is cleaned by contacting with an acidic cleaning solution in an acid cleaning step, preferably undergoing a post-rinse step prior to the immersion plating step.
- 15 14. A process according to any preceding claim in which prior to contacting the metal surface with the immersion plating composition, the metal surface undergoes a micro-etching step and preferably between the micro-etching step and the immersion plating step, there is an additional acid
20 rinse step.
15. A process according to claim 14 in which the acid rinse step is in addition to an acid cleaning step according to claim 13.
- 25 16. A process according to any preceding claim in which the displacement composition comprises a tarnish inhibitor.

Figure 1

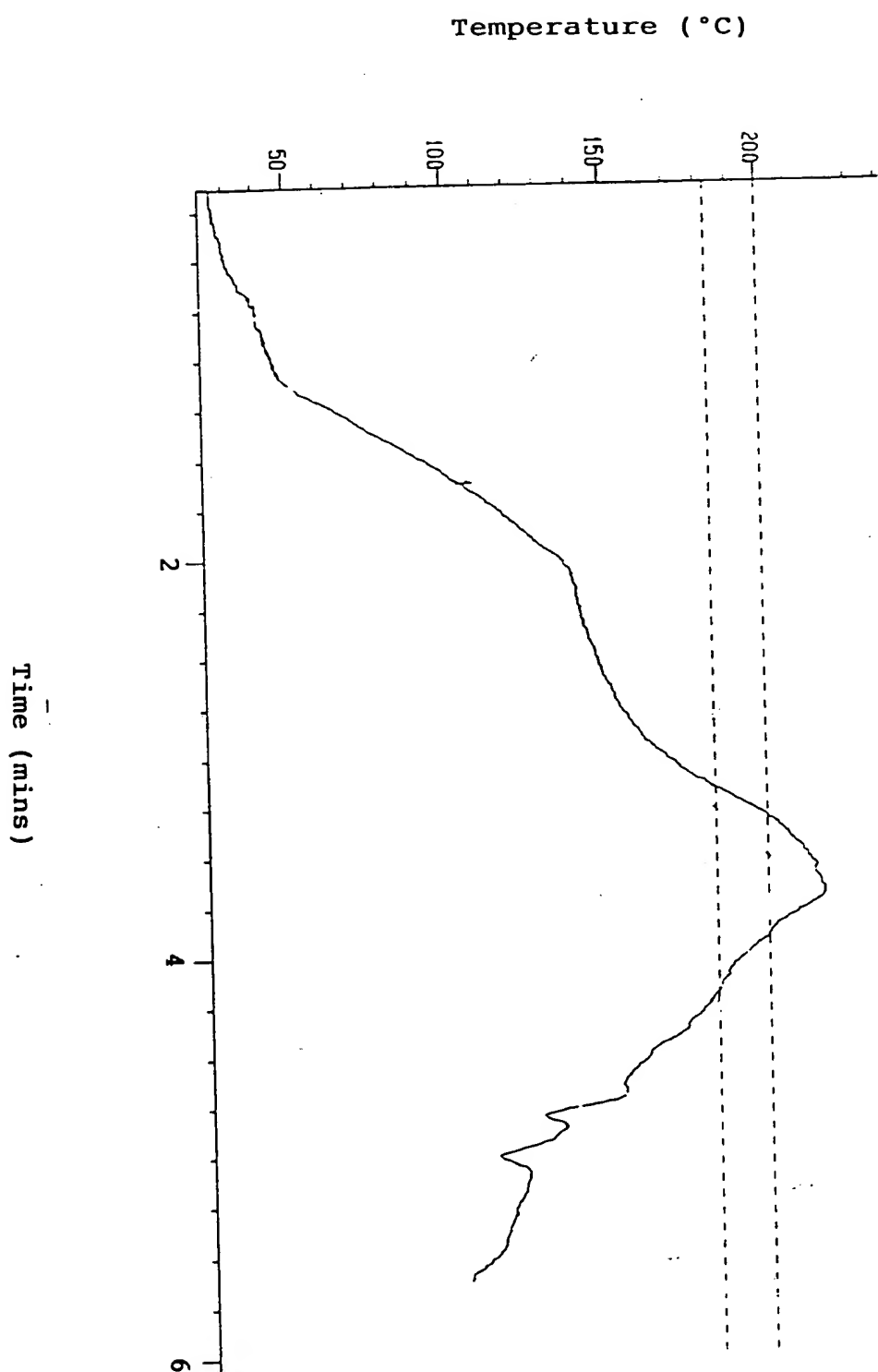


Figure 1

